View metadata, citation and similar papers at core.ac.uk

brought to you by CORE

provided by DigitalCommons@URI

Masthead Logo

University of Rhode Island
DigitalCommons@URI

Chemistry Faculty Publications

Chemistry

2016

Improved cycling performance of Si nanoparticle anodes via incorporation of methylene ethylene carbonate

Cao Cuong Nguyen
University of Rhode Island

Brett L. Lucht
University of Rhode Island, blucht@uri.edu

Creative Commons License
Creative Commons License
This work is licensed under a Creative Commons Attribution-Noncommercial-No Derivative Works 4.0 License.

Follow this and additional works at: https://digitalcommons.uri.edu/chm_facpubs

This is a pre-publication author manuscript of the final, published article.

Citation/Publisher Attribution
Nguyen, C. C., & Lucht, B. L. (2016). Improved cycling performance of Si nanoparticle anodes via incorporation of methylene ethylene carbonate. *Electrochemistry Communications, 66*, 71-74. doi: 10.1016/j.elecom.2016.03.005
Available at: https://doi.org/10.1016/j.elecom.2016.03.005

This Article is brought to you for free and open access by the Chemistry at DigitalCommons@URI. It has been accepted for inclusion in Chemistry Faculty Publications by an authorized administrator of DigitalCommons@URI. For more information, please contact digitalcommons@etal.uri.edu.

Improved cycling performance of Si nanoparticle anodes via incorporation of Methylene Ethylene Carbonate

Cao Cuong Nguyen and Brett L. Lucht*

Department of Chemistry, University of Rhode Island, Kingston, Rhode Island 02882, USA

* Correspondence Author:

Phone:1-401-874-5071

Fax: 1-401-874-5072

E-mail: blucht@chm.uri.edu

© 2016. This manuscript version is made available under the Elsevier user license
http://www.elsevier.com/open-access/userlicense/1.0/

Abstract

Methylene ethylene carbonate (MEC) has been investigated as an alternative additive to fluoroethylene carbonate (FEC) for Si nanoparticle anodes cycled with 1.2 M $LiPF_6$/ethylene carbonate (EC) : diethyl carbonate (DEC) (1:1, w/w) electrolyte. The Si electrodes cycled with 10% MEC-added electrolyte exhibit significantly improved capacity retention after 100 cycles compared to standard electrolyte (73% vs 46%). In addition, the Si electrode cycled with MEC additive has less damage from cracking than the standard electrolyte. Ex-situ surface analyses via infrared and X-ray photoelectron spectroscopy reveal a Solid Electrolyte Interphase (SEI) containing a high concentration of a poly(MEC), which is likely responsible for the improved performance of Si anodes.

Keyword: Silicon Anode, Electrolyte Additive, Methylene ethylene carbonate, Solid Electrolyte Interphase, Surface analysis

1. Introduction

Si has been intensively investigated as anode material for lithium ion batteries due to its high theoretical capacity of 3579 mAh/g, which is ten times higher than graphite anodes (372 mAh/g) [1]. However, the large volume change of Si anodes (~280%) upon cycling causes particle pulverization and loss of electrical connection within electrode components [1]. Another problem associated with the large volume change of Si particles is the repeated formation and destruction of the protective solid electrolyte interphase (SEI) which consumes active lithium. One efficient strategy to improve cycling performance of Si anodes is incorporation of electrolyte additives to generate a more stable SEI. Fluorothylene carbonate (FEC) is currently considered as the best additive for enhancing capacity retention of Si anodes [2,3]. FEC is reduced on the Si surface to form an SEI consisting of a combination of poly(FEC) and lithium salts such as lithium alkyl carbonate, lithium carbonate and lithium fluoride [3,4]. The use of silicon / graphite composite electrodes retain some of the increased capacity of silicon, but provide much better capacity retention upon cycling. However, recent investigations suggest that high concentrations of FEC increase the reactivity of the electrolyte with lithiated graphite resulting in large capacity loss [5]. The high concentration of FEC also causes significant gas evolution in Graphite / $LiCoO_2$ full cells compared to VC and standard electrolyte [6]. Finally, the cycling performance of Si-graphite / NCM111 full cells with 10% VC was found to be better than 10% FEC [7]. These problems hinder the practical use of Si-graphite composite electrodes in commercial cells since a high concentration of FEC is required to stablize the added silicon. The use of methylene ethylene carbonate (MEC, Fig. 1a) has been previously reported to significantly improve cycling performance of graphite / NCM111 cells at evalavated temperature

with no evidence of significant gas evolution [8,9]. The improvement is likely due to the formation of a high concentration of a polycarbonate derived from MEC, poly(MEC), on the electrode surface.

Herein, we report effects of MEC on cycling ability, surface chemistry and morphology changes of Si electrodes utilizing charge-discharge cycling, field-emission scanning electron microscopy (FE-SEM), attenuated total reflection infrared (ATR IR) and X-ray photoelectron spectroscopy (XPS).

2. Experimental

Silicon (≤ 50nm, Alfar Aeasar), super C (Timcal) and sodium carboxymethyl cellulose (CMC, 7000,000, Aldrich) and poly(acrylic acid) (PAA, 450,000, Aldrich) with a ratio of 50 : 25: 12.5 : 12.5 (in weight) [10] were thorough mixed in distilled water. The well mixed slurry was spread on copper foil and dried in air. The electrodes were then punched into 14.0 mm diameter disks and dried at 110 ^{o}C in a vacuum oven for 6 hrs, followed by another 4 hrs at 150^{0}C. The electrode loading is ~1 mg of Si/cm^{2}.

Solvents, salts and additives were obtained from BASF and used as received. 2032 coin cells consist of a Si working electrode, a lithium foil counter electrode, 100 µl of electrolyte and two separators (one Celgard 2325 and one Whatman GF/D glass fiber). The standard electrolyte was 1.2M $LiPF_6$/EC : DEC (1:1, w/w). MEC and FEC were added into standard electrolyte with 5 – 10 wt.%. The cells were charged (lithiation) and discharged (delithiation) between 0.005 and 1.5 V with constant-current and constant voltage (CC-CV) at a rate of C/20 for first cycle and C/3 for an additional 99 cycles using an Arbin BT2000 battery cycler at 25^{o}C. At the end of lithiation, the voltage of the cells was held at 0.005 V until the current decreases to C/40 for first

cycle and C/20 for the subsequent cycles. The rate was calculated based on the theoretical capacity of Si at 3579 mAh/g.

Prior to ex-situ analysis, cycled electrodes (100^{th} delithiation) were carefully rinsed with DMC four times (1 mL in total) to remove residual electrolyte and then dried in a glove box. Infrared spectra with attenuated total reflectance (IR-ATR) were measured with 512 scans and a spectral resolution of 4 cm^{-1} using a Bruker Tensor 27 equipped with LaDTG detector inside a nitrogen-filled glovebox. Surface compositional analysis was conducted using ex-situ XPS (K-alpha, Thermo) with Al K_α X-ray source and measured spot size of 400 μm. The electrodes were transferred from the glove box to the XPS analysis chamber using a special vacuum-sealed module (Thermo) without exposure to air at any time. The binding energy was corrected based on the C 1s of hydrocarbon at 285 eV. The change in surface morphology before and after cycling was examined by ex situ SEM (Sigma VP, Zeiss Carl).

3. Results and Discussions

The electrochemical cycling data of Si / Li cells cycled with standard electrolyte with and without added MEC are presented in **Fig. 1b-f**. The cycling data of Si with 10% FEC are also included for comparison. All cells show similar initial voltage profiles with initial delithiation capacity of about 3600 mAh/g, based on weight of silicon (Fig 2.b). The dQ/dV plots for the first charge (Fig. 1c) for cells cycled with standard electrolyte exhibit peaks at ~ 0.9 and 0.65 V due to the reduction of EC and DEC [11]. An additional peak is observed at ~1.6 V is likely from the reduction of the hydroxyl groups of the PAA and CMC binders. The cell cycled with 10% of added MEC contains an additional new peak at ~1 V, which is likely due to the reduction of MEC, forming poly(MEC) as previously reported [8]. The electrode cycled with standard electrolyte has rapid capacity fade to 1500 mAh/g, corresponding to 46% capacity retention (Fig

2d and e), over the first 100 cycles. Addition of MEC into the standard electrolyte dramatically improves both capacity retention and efficiency. The cells cycled with 10% MEC exhibit excellent capacity retention (73%) and high specific capacity of ~ 2500 mAh/g after 100 cycles, which is slightly better than cells containing 10% FEC (Fig. 1d and e). Furthermore, the first cycle efficiency of the cells containing 10% MEC is higher than cells containing 10% FEC (Fig. 1f). In addition, the charge and discharge curves of the cells cycled with 10% MEC after 100 cycles are very similar to the charge discharge curves for the cells cycled with 10% FEC (Fig. 1d), suggesting that cell impedance is similar.

The IR spectra of fresh and cycled Si anodes are provided in **Fig. 2**. The fresh electrode contains strong absorptions at 1717 and 1572 cm^{-1} due to carboxylic acids and carboxylate salts from PAA and CMC binders. The peaks in region of 1250-950 cm^{-1} are from stretching vibrations of surface silicon oxide, SiO_x, and -C-O- bonds from binders [4,10]. After cycling with the standard electrolyte, the spectrum is dominated by new peaks at 1653, 1325 and 825 cm^{-1}, attributed to lithium alkyl carbonates ROCOOLi, and at 1489 and 871 cm^{-1} from lithium carbonate Li_2CO_3 [3,4]. The IR spectrum of the Si electrode cycled in 10% MEC also contains absorptions characteristic of Li_2CO_3 but the peaks characteristic of lithium alkyl carbonates (ROCOOLi) at ~1650 cm^{-1} are significantly diminished. New peaks are observed characteristic of lithium carboxylates at 1610 cm^{-1} and poly(MEC) at 1809 and 1067 cm^{-1} [3,8]. The MEC derived SEI appears to suppress the reduction of the carbonate solvents.

The C1s and O1s XPS spectra for fresh and cycled Si electrodes are provided in **Fig. 3**. The fresh electrode has a peak at ~ 284 eV, attributed to super C and peaks at 285, 286.5 and 288.7 eV ascribed to C-C, -C-O and $-CO_2$ groups present in the binders. The O 1s spectrum of the fresh electrode has a broad peak centered at 532.4 eV characteristic of a mixture of Si-O, C-

O, and C=O bonds. After cycling, the intensity of both the C 1s and O 1s peaks significantly increase, supporting the formation of a thick SEI on those electrodes composed of the reduction products of the electrolyte. The C1s spectrum of the electrode cycled with standard electrolyte has strong peaks at 290 and 286.5 eV, and related peaks are observed in the O1s spectrum at 531.5 and 533 eV characteristic of C=O, and C-O bonds, respectively. The data is consistent with an outer SEI primarily composed of lithium alkyl carbonates and Li_2CO_3 [3,12]. The C1s spectrum of the electrode cycled with electrolyte containing 10% MEC is similar, but the peak at 286.5 eV has greater intensity consistent with more C-O species present in the SEI. The O1s spectrum has a related increase in the intensity of the peak 533 eV consistent with higher concentration of C-O containing species. The related shoulder has also been reported in support of the presence of polycarbonate [3]. The F 1s and P 2p XPS spectra are similar for all samples. The XPS spectra are consistent with the IR spectra and suggest that the SEI on the electrode cycled in 10% MEC is primarily composed of poly(MEC) with lower concentrations of lithium carbonate and lithium carboxylate.

The morphology changes of electrodes before and after cycling were examined by FE-SEM and depicted in **Fig. 4**. The fresh Si electrode has a smooth surface. After cycling with the standard electrolyte, large cracks are observed which are likely related to the poor cycling performance as seen in **Fig. 1**. The electrode cycled with the electrolyte containing 10% MEC also results in cracking but the crack size is smaller. The high concentration of poly(MEC) in the SEI appears to effectively inhibit electrode damage from the large volume changes of silicon during cycling, resulting in significant improvement in capacity retention as shown in **Fig**. **1e**.

4. Conclusion

The electrolyte additive MEC significantly improves both capacity retention and efficiency of Si nanoparticle electrodes. The electrode cycled with electrolyte containing MEC has superior capacity retention to the electrode cycled with the standard electrolyte, 73% compared to 46% after 100 cycles. The IR and XPS data suggest that the electrode cycled with electrolyte containing MEC has an SEI primality composed of poly(MEC), Li_2CO_3, and lithium carboxylate, with a significantly lower concentration of lithium alkyl carbonates. The high concentration of poly(MEC) appears to suppress the reduction of electrolyte solvents and inhibit silicon nanoparticle electrode damage from the large volume changes during the cycling of Si in a similar fashion to that reported for poly(FEC) [4]. MEC is an excellent alternative to FEC for Si nanoparticle electrodes.

Acknowledgements

The authors gratefully acknowledge funding from Department of Energy Office of Basic Energy Sciences EPSCoR Implementation award (DE-SC0007074)

References

[1] M.N. Obrovac, L.J. Krause, Reversible Cycling of Crystalline Silicon Powder, J. Electrochem. Soc. 154 (2007) A103–A108.

[2] N.-S. Choi, K.H. Yew, K.Y. Lee, M. Sung, H. Kim, S.-S. Kim, Effect of fluoroethylene carbonate additive on interfacial properties of silicon thin-film electrode, J. Power Sources. 161 (2006) 1254–1259.

[3] V. Etacheri, O. Haik, Y. Goffer, G. a Roberts, I.C. Stefan, R. Fasching, D. Aurbach, Effect of Fluoroethylene Carbonate (FEC) on the Performance and Surface Chemistry of Si-Nanowire Li-Ion Battery Anodes, Langmuir. 28 (2011) 965–976.

[4] C.C. Nguyen, B.L. Lucht, Comparative Study of Fluoroethylene Carbonate and Vinylene Carbonate for Silicon Anodes in Lithium Ion Batteries, J. Electrochem. Soc. 161 (2014) A1933–A1938.

[5] L. Ma, J. Xia, X. Xia, J.R. Dahn, The Impact of Vinylene Carbonate, Fluoroethylene Carbonate and Vinyl Ethylene Carbonate Electrolyte Additives on Electrode/Electrolyte Reactivity Studied Using Accelerating Rate Calorimetry, J. Electrochem. Soc. 161 (2014) A1495–A1498.

[6] D.Y. Wang, N.N. Sinha, J.C. Burns, C.P. Aiken, R. Petibon, J.R. Dahn, A Comparative Study of Vinylene Carbonate and Fluoroethylene Carbonate Additives for LiCoO2/Graphite Pouch Cells, J. Electrochem. Soc. 161 (2014) A467–A472.

[7] S.E. Trask, K.Z. Pupek, J.A. Gilbert, M. Klett, B.J. Polzin, A.N. Jansen, D.P. Abraham, Performance of Full Cells Containing Carbonate-Based LiFSI Electrolytes and Silicon-Graphite Negative Electrodes, J. Electrochem. Soc. 163 (2016) A345–A350.

[8] D. Chalasani, J. Li, N.M. Jackson, M. Payne, B.L. Lucht, Methylene ethylene carbonate: Novel additive to improve the high temperature performance of lithium ion batteries, J. Power Sources. 208 (2012) 67–73.

[9] W. Xu, P. Bolomey, M.W. Payne, Non-Aqueous Electrolytic Solutions And Electrochemical Cells Comprising The Same, US20090017386 A1, 2009.

[10] B. Koo, H. Kim, Y. Cho, K.T. Lee, N.-S. Choi, J. Cho, A Highly Cross-Linked Polymeric Binder for High-Performance Silicon Negative Electrodes in Lithium Ion Batteries, Angew. Chem. Int. Ed. 51 (2012) 8762–8767.

[11] X. Zhang, R. Kostecki, T.J. Richardson, J.K. Pugh, P.N. Ross, Electrochemical and Infrared Studies of the Reduction of Organic Carbonates, J. Electrochem. Soc. 148 (2001) A1341–A1345.

[12] R. Dedryvère, L. Gireaud, S. Grugeon, S. Laruelle, J.-M.M. Tarascon, D. Gonbeau, R. Dedryvere, Characterization of Lithium Alkyl Carbonates by X-ray Photoelectron Spectroscopy: Experimental and Theoretical Study, J. Phys. Chem. B. 109 (2005) 15868–15875.

Figure captions

Fig. 1. Structure of methylene ethylene carbonate (MEC) (a), voltage profiles (b) and their differential capacity plots (c) for first cycle, voltage profiles after 100 cycles (d), capacity retention (e) and coulombic efficiency (f) as a function of cycle number of Si electrodes in different electrolytes.

Fig. 2. ATR-IR of Si electrodes before and after 100 cycles.

Fig. 3. C 1s and O 1s XPS spectra of Si electrodes before and after 100 cycles.

Fig. 4. SEM images for fresh electrode (a) and electrodes after 100 cycles in standard electrolyte (b) and 10 % MEC (c).

Figures

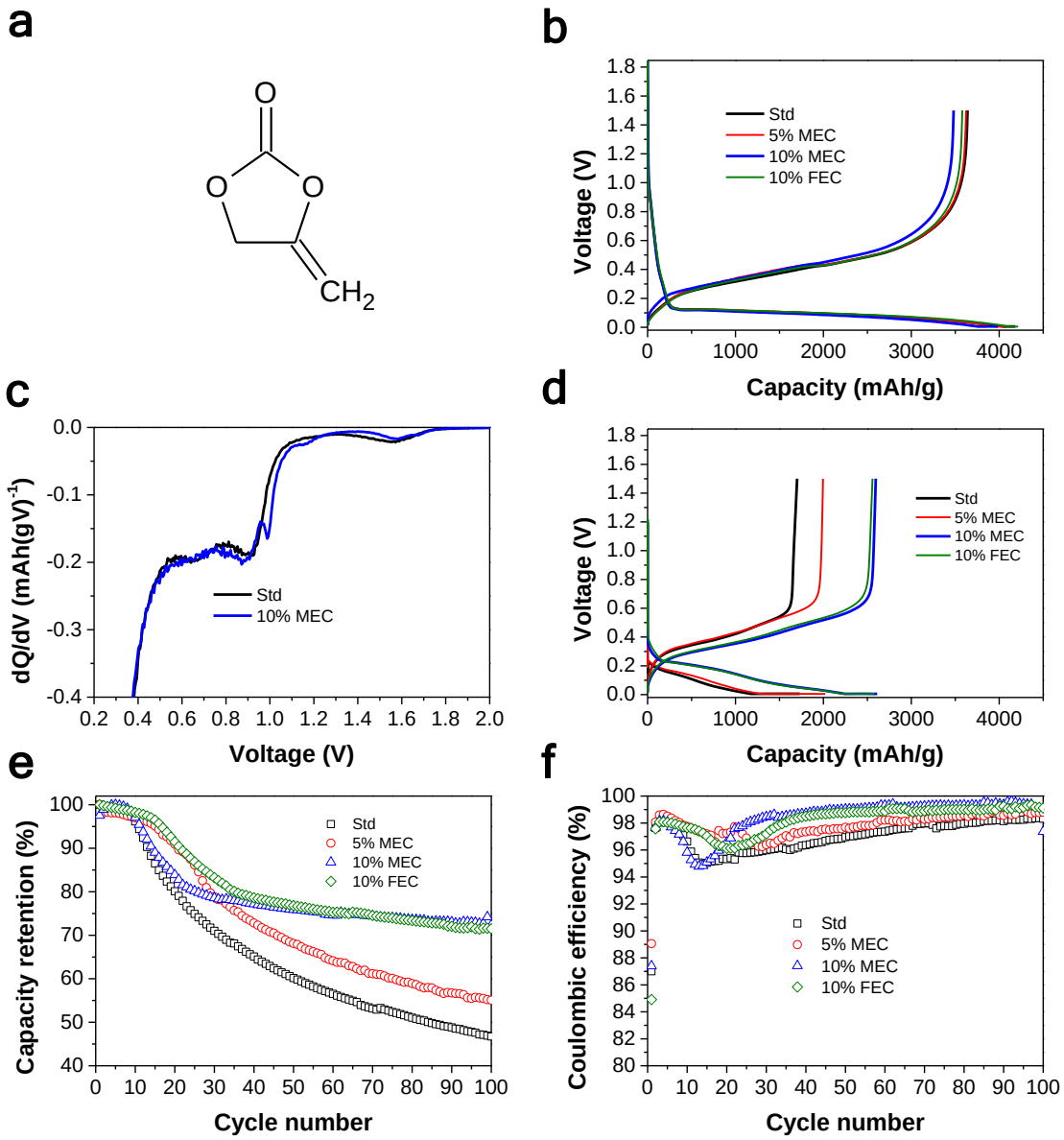

Fig. 1. Structure of methylene ethylene carbonate (MEC) (a), voltage profiles (b) and their differential capacity plots (c) for first cycle, voltage profiles after 100 cycles (d), capacity retention (e) and coulombic efficiency (f) as a function of cycle number of Si electrodes in different electrolytes.

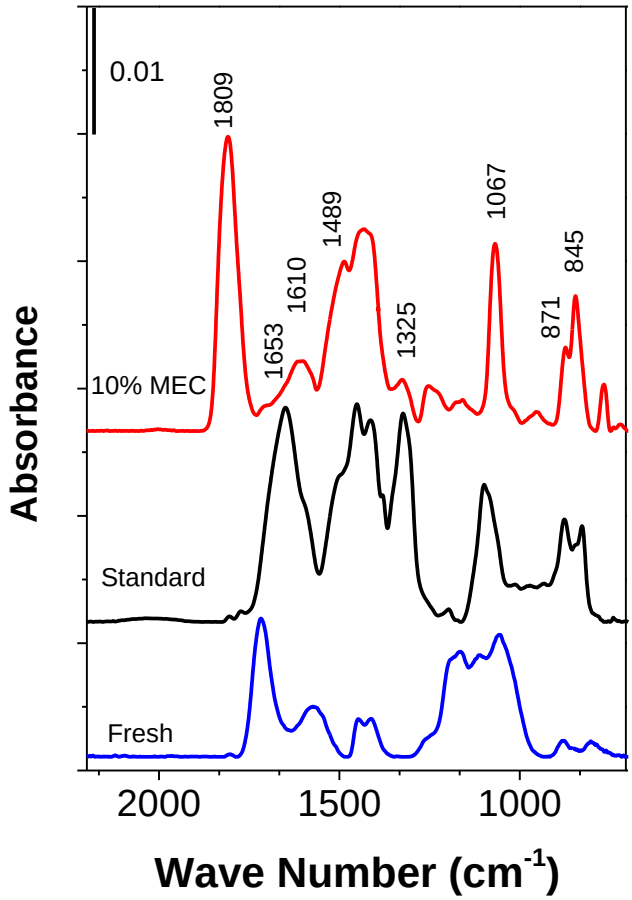

Fig. 2. ATR-IR of Si electrodes before and after 100 cycles.

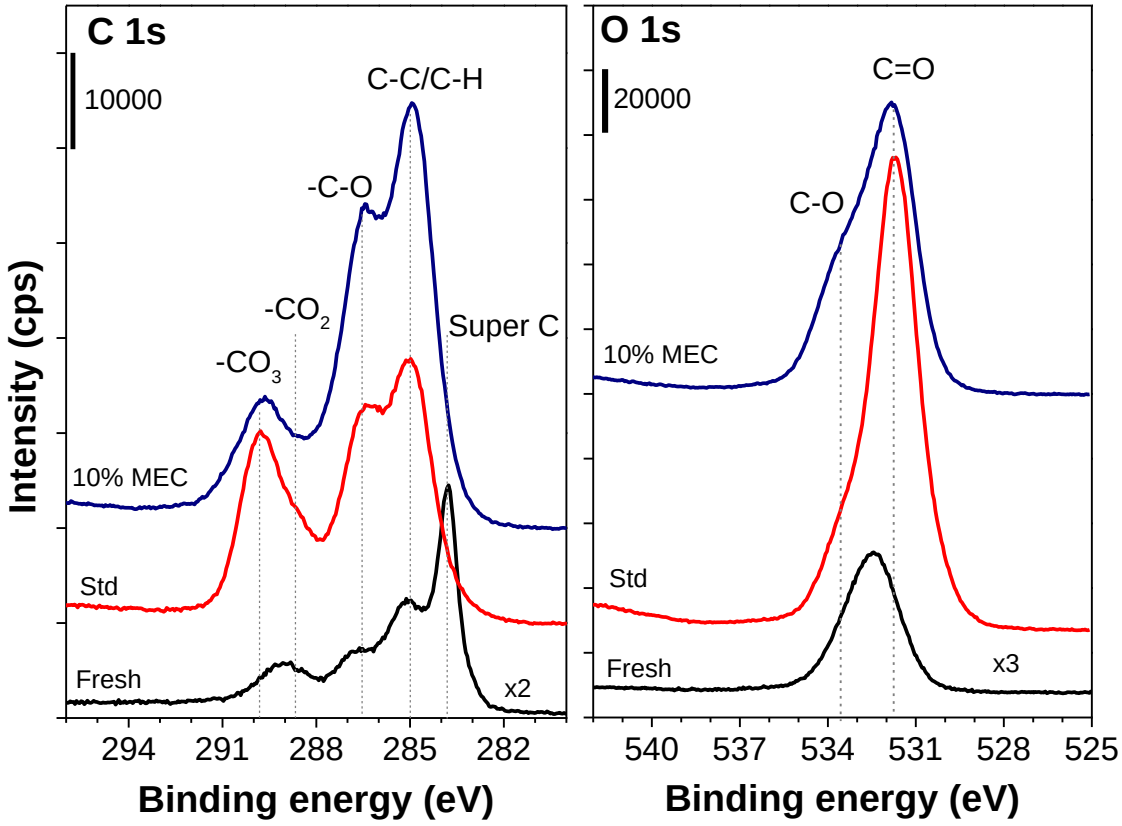

Fig. 3. C 1s and O 1s XPS spectra of Si electrodes before and after 100 cycles.

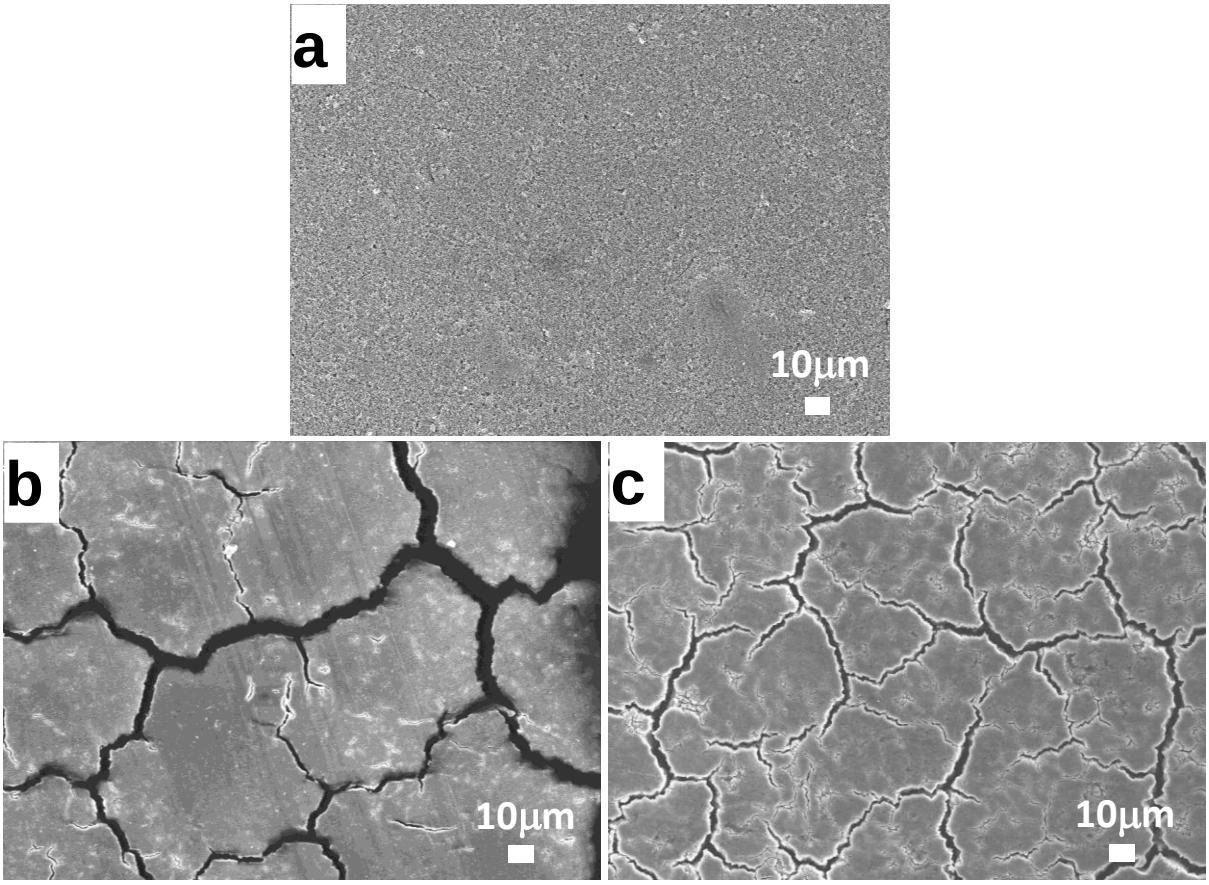

Fig. 4. SEM images for fresh electrode (a) and electrodes after 100 cycles in standard electrolyte (b) and 10 % MEC (c).

Graphical abstract